

Synthesis and Spectral Study of 2-furaldehyde Thiourea Ligand and Their Complexes with Some Transition Metal (II)

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Abstract

The synthesis and characterisation of $\text{Ni}^{(II)}$, $\text{Cu}^{(II)}$ of 2-furaldehyde thiourea (FAT) are reported. Elemental analysis, molar conductance and spectral (IR, UV and ^1H NMR) measurements have been used to characterise the complexes. In addition, the structure of the complex $[\text{Cu}(\text{FAT})_2]\text{Cl}_2$ has been determined by X-ray diffraction methods. In $\text{Cu}^{(II)}$ and $\text{Ni}^{(II)}$ complexes, the metal ion is coordinated through the sulfur atom and the azomethine nitrogen atom.

Keywords: thiourea, Furfural, 2-furaldehyde thiourea; metal complexes,.

1. Introduction

Thiourea, their derivatives, as well as their transition metal complexes have aroused considerable interest in the areas of chemistry and biology. These compounds present a wide variety of biological activity such as antitumoral ^[1,8], fungicidal ^[9,10], bactericidal ^[11] or antiviral ^[12,13]. They have been used for metals analyses ^[14], for device applications relative to telecommunications, optical computing, storage and information processing ^[15,16]. As part of our continuous research work about synthesis and biological activity, mainly with thiourea and semicarbazones deriving from furfuraldehyde and their metal complexes ^[17-21], we describe in this work a new series of transition metal complexes obtained from 2-furaldehyde thiourea FAT as ligand and the chlorides of $\text{Ni}^{(II)}$, $\text{Cu}^{(II)}$.

All structures are determined on the basis of elemental analyses and spectroscopic techniques. In addition, the crystal structure of the copper complex $[\text{Cu}(\text{FAT})_2]$ and is described.

2. Experimental

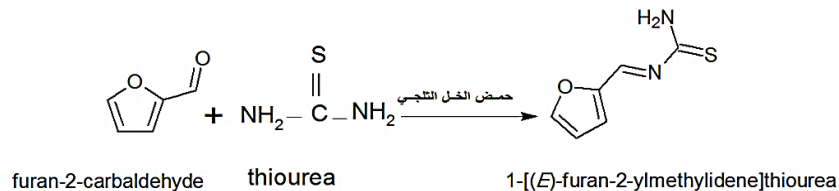
2-1- materials & tools

- ❖ Melting points were determined by using a micro-melting point apparatus without any corrections.
- ❖ Infra Red spectra pattern FT-IR-410 produce Jasco – Japan . reported relative in KBr stretch bonds in cm^{-1} .
- ❖ spectrum NMR proton and carbon device 400 MHz model Bruker by Switzerland company .
- ❖ A spectral analysis of metals on the principle of optical spark electric version of the company Oxford Instruments in the Department of Physics - Faculty of Science - University of the expedition.
- ❖ All chemical materials from Sigma Aldrich.

2-2-Preparation of the ligand (FAT):

The 2-furaldehyde thiourea was synthesised as previously described [11] by refluxing 2-furaldehyde and thiourea (1:1 molar ratio) in absolute ethanol in the presence of pure acetic acid.

The mixture was refluxed for 12 h and then cooled, filtered and recrystallised from a mixture of ethanol (75% V/V) and water. Yellow microcrystalline products are obtained.(yield 45%, melting point = 154-155 °C).



Scheme 1: Reaction of thiourea with furfural

2-3-General Synthesis of metal Complexes;

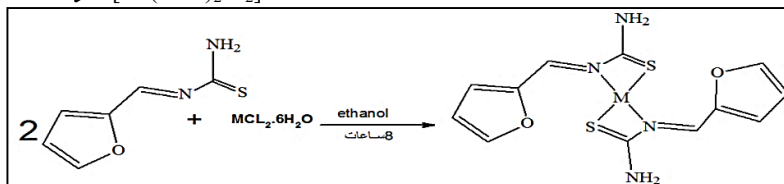
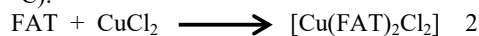
2.3.1. Bis(2-furaldehydethiourea)nickel (II) $[\text{Ni}(\text{FAT})_2]\text{Cl}_2$:

The hexahydrated nickel chloride, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (2.5×10^{-3} mol, 0.59 g), was dissolved in distilled water. An ethanolic solution of FTSC (5×10^{-3} mol; 0.85 g, 10mL) was added slowly while stirring. The mixture was refluxed for 6 h. After cooling at room temperature, a green precipitate appeared. It was filtered, washed with small amounts of absolute ethanol and finally dried in vacuum over silica gel. All the compounds were washed and dried in the same way. (yield 25%, melting point = 235 °C).



2.3.2. Bis(2-furaldehydethiourea)copper (II) [Cu(FAT)₂]Cl₂:

When 2×10^{-3} g of complex [Cu (FAT)₂]cl₂ was dissolved in ethanol (20 mL), a dark-green crystalline product of formula [Cu(FAT)₂]cl₂ was isolated after several days at room temperature. (yield 20%, melting point = 210 °C).



Scheme 2: Reaction of metal complex:

Table1: show Some properties of the synthesized of 2-furaldehyde thiourea and metal complex

Compounds	Formulas	Color	m.p ^o C	Yield (%)
FAT(L)	C ₆ H ₆ N ₂ OS	yellow	154-155	45
[Ni(FAT) ₂]Cl ₂	C ₁₂ H ₁₂ N ₄ O ₂ S ₂ NiCl ₂	green	235-dec	25
[Cu(FAT) ₂]Cl ₂	C ₁₂ H ₁₂ N ₄ O ₂ S ₂ CuCl ₂	green	210-dec	20

3. Results and Discussion and Discussion

3-1- IR spectra of the (APH) ligand and their complexes:

The infrared spectra for the present compounds taken in the range 400-4000 cm⁻¹ help to indicate regions of absorption vibrations. The main stretching modes are for ν(C=N), ν(C=C). The IR data of the spectra of ligands (FAT) and their complexes are presented in Table 2. The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation.

Spectrum of the FAT ligand shows a sharp band at (1600cm⁻¹) due to ν(C=N) azomethine group which has shifted to higher frequency about (50cm⁻¹) in the complexes indicating its participation in chelation through azomethine nitrogen. The height of band is due to the reduction of electron density in the azomethine link. furfural ν(C=S) shows absorption band at (1100cm⁻¹) in the ligand spectrum. These band rises shift by (1050cm⁻¹) in the complex. Azomethine group in the FAT hanged after complication .with Ni^(II) from (1600cm⁻¹) to (1650cm⁻¹) this indicate that involvement of Azomethine group in complications.

Table 2. Characteristic infrared absorption frequencies (cm⁻¹) of the ligand and complexes.

compounds	ν(NH)	ν(C=N)	ν(C=S)	ν(C-H)SP ²	ν(C-H)Sp ³
FAT	3300 _{st}	1600 _{st}	1100 _m	3194 _w	2925 _w
[Ni(FAT) ₂]Cl ₂	3412 _{st}	1650 _{st}	1050 _m	3069 _w	2930 _w
[Cu(FAT) ₂]Cl ₂	3400 _{st}	1667 _{st}	1010 _m	3126 _w	3008 _w

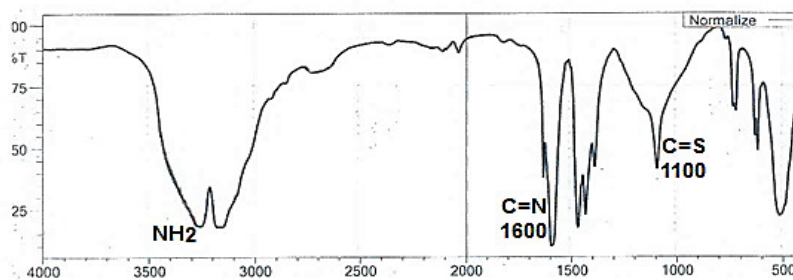


Figure 1: IR spectrum of ligand (FAT)

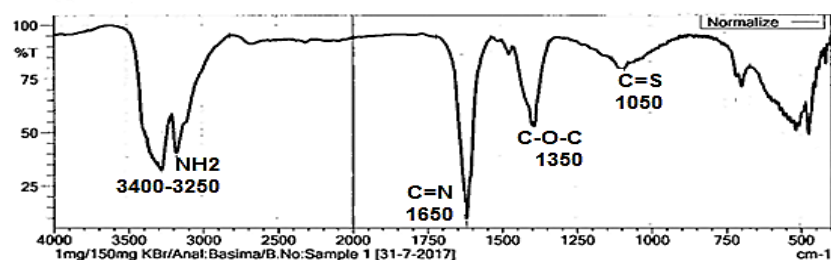


Figure 2: IR spectrum of complex $[\text{Ni}(\text{FAT})_2]\text{Cl}_2$

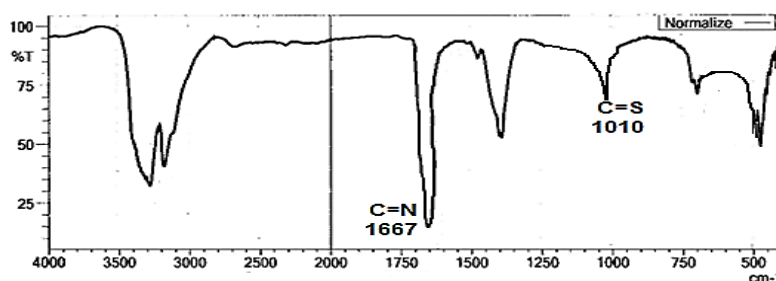


Figure 3: IR spectrum of complex $[\text{Cu}(\text{FAT})_2]\text{Cl}_2$

3.2. Electronic spectral data:

The data of the electronic spectra of the ligand and its complexes are given in Table 3. The spectrum of Schiff base (FAT) presented two bands in the UV interval at 235nm and 290nm, assigned to ($\pi \rightarrow \pi^*$) and ($n \rightarrow \pi^*$) transitions respectively.

The electronic spectra of the complexes in methanol solution has three bands at (220,300,356)nm. These bands may be assigned to the charge transitions (LMTC) of the form ($n \rightarrow \pi^*$) for azomethine group ($\text{C}=\text{N}$). The position of these bands suggests an octahedral environment to $\text{Ni}^{(\text{II})}$, $\text{Cu}^{(\text{II})}$.

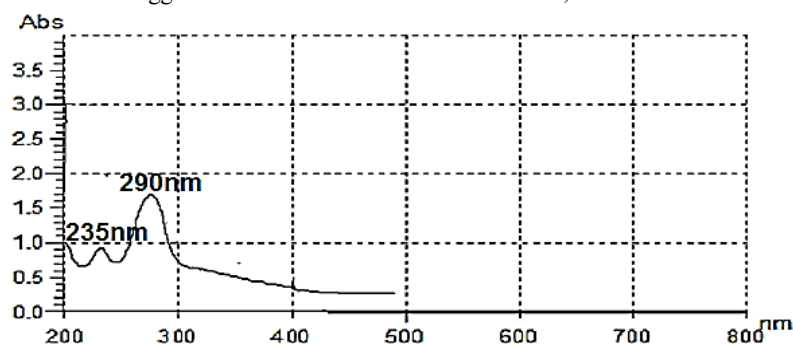


Figure 4: UV absorption spectrum of ligand (FAT)

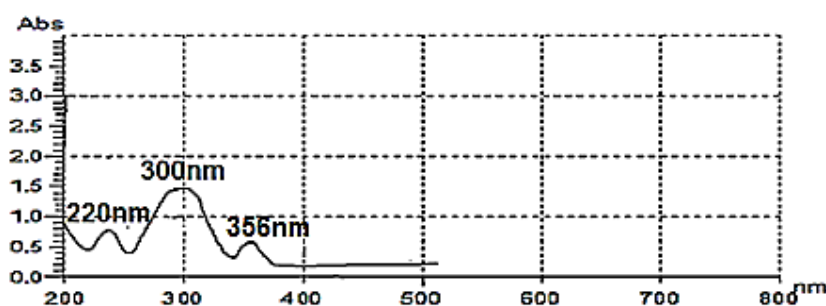


Figure 5: UV absorption spectrum of $[\text{Ni}(\text{FAT})_2]\text{Cl}_2$

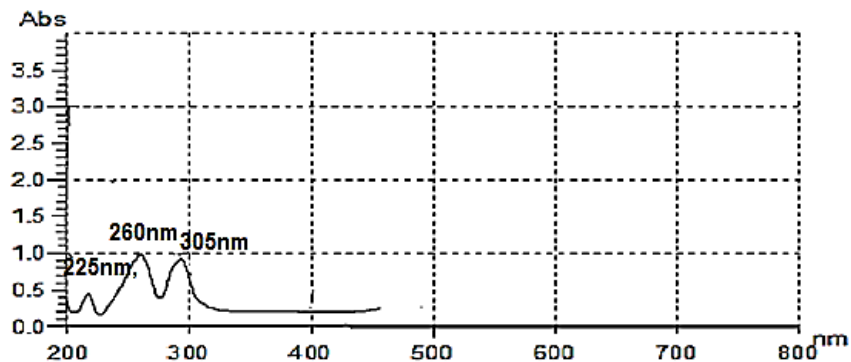
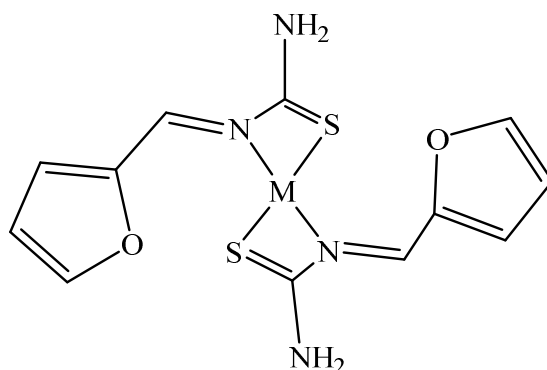


Figure 6: UV absorption spectrum of $[\text{Cu}(\text{FAT})_2]\text{Cl}_2$

Table 3: Magnetic moments, electronic bands and ligand filed parameters of FAT and its metal complexes ^[16].

compound	$\pi \rightarrow \pi^*$ (nm)	$n \rightarrow \pi^*$ (nm)	$L \rightarrow M$ (nm)
FAT	235	290	---
$\text{Ni}(\text{FAT})_2\text{Cl}_2$	220	300	.356
$\text{Cu}(\text{FAT})_2\text{Cl}_2$	225	260	305



Scheme 1: Suggested structures for the FAT complexes

3.3. ¹H-NMR spectroscopic measurements:

(¹H-NMR) spectra of the ligand FAT.

The (¹H-NMR) spectroscopic measurement of FAT are given in Table 4.

Table 4. The (¹H-NMR) spectroscopic measurement of FAT.

J [Hz]	chemical shift [PPM]	proton number	
-	3.336	(1H,S)	1
5	8.005	(1H,d)	2
5	6.525	(1H,t)	3
5	7.699	(1H,d)	4
5	8.772	(1H,S)	6
5	7.002	(2H,S)	8 (NH ₂)

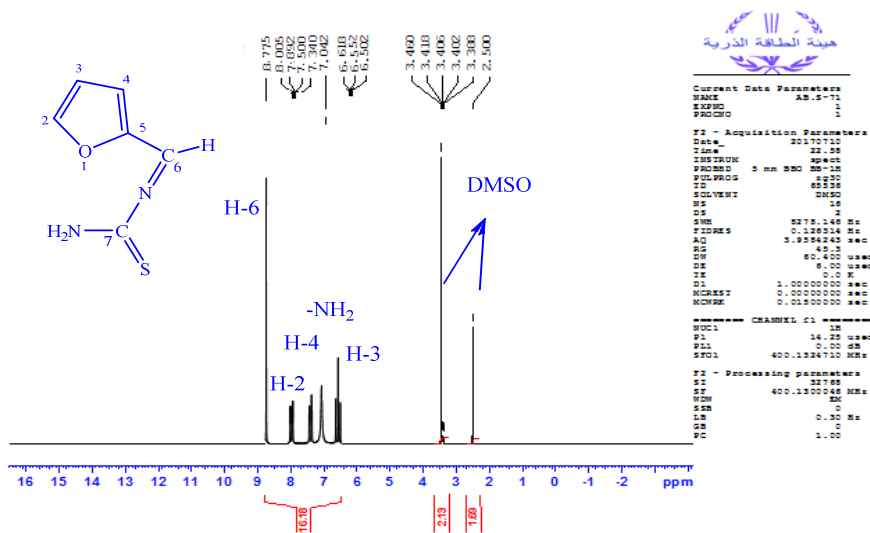


Figure 7 : ¹H NMR spectrum of FAT

3.4. Electronic microscope spectroscopic measurements :

Electronic microscope spectrum of FAT and complex $[\text{Cu}(\text{FAT})_2]\text{Cl}_2$.

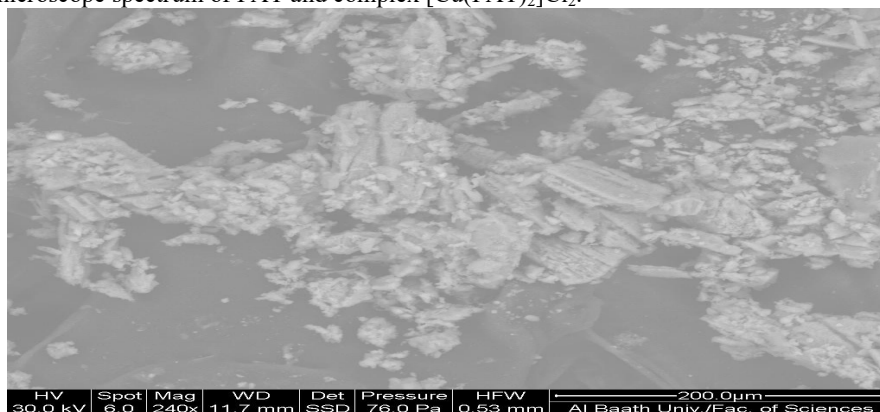


Figure 8 : Electronic microscope spectrum of FAT

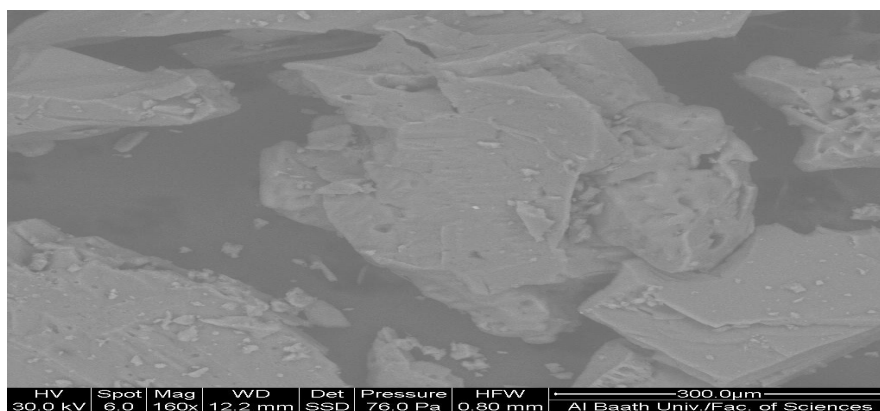


Figure 9 : Electronic microscope spectrum of complex $[\text{Cu}(\text{FAT})_2]\text{Cl}_2$

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